RAPID PUBLICATION

Formation of Intermetallic Compounds Layer Composed of Ni_3Y and Ni_5Y by Electrodeposition on Ni Using Molten NaCl-KCl-YCl_3

Yoshiyuki Sato and Motoi Hara

Department of Materials Engineering and Applied Chemistry, Mining College, Akita University,
1-1, Tegata Gakuen-machi, Akita 010, Japan

Electrodeposition of Y on Ni and their alloying by molten salt electrolysis was attempted in an equimolar NaCl-KCl melt containing up to 4 mol% YCl_3 at 1073 K. The electrolysis was carried out using the potentiostatic polarization method at constant potentials of -1.8 , -2.0 and -2.2 V vs. $\text{Ag/AgCl}(0.1)$ for 1.8 ks. In the potential region below -2.0 V in 49 mol% NaCl -49 mol% KCl -2 mol% YCl_3 , a dense, smooth and adhesive monolayer of about 30–120 μm thickness was formed on the Ni specimen. The polarization at less noble potential led to an increase in the thickness of the deposit layer. The layer consisted of intermetallic compounds of Ni_3Y and Ni_5Y . The Ni_3Y formed a matrix of the deposit layer, and the Ni_5Y formed a thin layer along the substrate/deposit interface and particles in the Ni_3Y matrix. The formation of such a layer was thought to result from the fact that reduction of the Y^{3+} ion proceeded effectively at the stated conditions and the reduced Y and Ni diffused into each other to form the intermetallic compounds layer.

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I. Introduction

Molten salt electrolysis is one of the effective methods for surface improvement. This electrolysis is advantageous to the deposition of refractory metals and rare earth metals, whose electrodeposition potentials are less noble than the reduction potential of H_2O , because the molten salts contain no H_2O and consequently in these electrolytes no hydrogen evolution due to H_2O reduction occurs. The molten salt electrolysis also enables alloying between the deposit and substrate because of a high temperature process.

On the other hand, it is well known that the addition of a small amount of rare earth metal into alloys improves high temperature oxidation resistivity of the alloys⁽¹⁾. Therefore, the deposition of rare earth metals, and their alloying with a metal substrate by molten salt electrolysis at high temperature has been expected to allow the preparation of a high temperature oxidation resistant surface.

Tamura *et al.*⁽²⁾ have succeeded in forming a LaNi_5 film on Ni by the electrodeposition of La in a KCl-LiCl eutectic melt with 10 mol% LaCl_3 at 773–923 K using galvanostatic electrolysis. Xie *et al.*⁽³⁾ has already developed a method to produce a Ni_2Y intermetallic compound film by galvanostatic electrolysis in a LiCl-KCl-NaCl eutectic melt containing 1.2 mol% YCl_3 at 723–973 K. During their study, a deposited Y formed the intermetallic Ni_2Y film on the Ni substrate. Tateiwa *et al.*⁽⁴⁾ has reported

about an advanced research concerning with the phase control of Ni_2Y intermetallic compound film formed by the electrodeposition using a LiCl-KCl eutectic melt with 0.17 mol% YCl_3 at 773 K, and its transformation into a porous structure.

In this study, the deposition of Y on Ni by potentiostatic polarization method and its simultaneous alloying with Ni have been attempted using a NaCl-KCl-YCl_3 melt at 1073 K. A particular attention was paid to the effect of polarization potential on the morphology of the deposit films. As a result, intermetallic compounds film consisting of Ni_3Y and Ni_5Y , that is smooth, uniform, and adhesive with Ni substrate, has been produced.

II. Experimental

The salt used as an electrolyte was an equimolar NaCl-KCl melt containing from 1 to 4 mol% YCl_3 . Commercial NaCl and KCl reagents were dehydrated by heating at 473 K for 86.4 ks in a vacuum. In order to use YCl_3 (Reagent class, Soekawa Chemicals, Co., Ltd.), a special effort not to hydrate it was required. The electrolyte was prepared from these NaCl , KCl and YCl_3 . The electrolysis was carried out using the potentiostatic polarization method with 3 electrodes. Figure 1 shows the experimental setup for electrodeposition. A pure Ni sheet (99.6 mass%) cut into a 10 mm $\times$ 10 mm $\times$ 1 mm coupon was used as the working electrode. A graphite rod of 5 mm diameter was used as the counter electrode. The reference electrode was a Ag wire immersed in an equimolar NaCl-

Fig. 1 Experimental setup for electrolysis in molten salt at 1073 K.

KCl melt containing 10 mol% AgCl placed in a mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) tube. The electrolyte was melted under an Ar atmosphere. The Ar gas was blown on the surface of the electrolyte at the rate of $3.3 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. In order to start the electrodeposition, Ni specimens were potentiostatically polarized at various cathodic potentials for 1.8 ks in the electrolyte at 1073 K. Cathodic polarization curves were also measured using the potential-sweeping method with a sweep rate of $1.67 \times 10^{-3} \text{ Vs}^{-1}$. After the electrodeposition, the surface of the specimen was washed with water, dried and analyzed by EPMA and XRD.

III. Results

Figure 2 shows the cathodic polarization curves of Ni measured in molten NaCl-KCl containing 1, 2, 3 and 4 mol% YCl_3 at 1073 K. For comparison, the figure includes the curve measured in molten NaCl-KCl without

Fig. 2 Cathodic polarization curves of Ni measured in NaCl-KCl- x mol% YCl_3 ($x=0, 1, 2, 3$ and 4) at 1073 K.

YCl_3 . For the melts containing YCl_3 , sharp increases in the cathodic current densities were observed in the potential region less noble than about -1.8 V . These increases in the cathodic current density seems to be due to reduction of the Y^{3+} ion.

It is because that the sharp increase in current density was observed only in YCl_3 -containing melts.

On the contrary, the cathodic limiting currents observed in the potential region from the rest potential to about -1.7 V are thought to correspond to the reduction of impurities in the melt such as H_2O because of their very small value. From this result, it is obvious that Y^{3+} reduction occurs in the potential region less noble than about -1.8 V .

According to the cathodic polarization curve results, the electrodeposition was carried out by the potentiostatic polarization at -1.8 , -2.0 and -2.2 V in 49 mol% NaCl-49 mol% KCl-2 mol% YCl_3 at 1073 K for 1.8 ks. Figure 3 shows the time dependence of current densities during the electrodeposition. Almost constant cathodic current densities are observed at each potential. The cathodic current density increases with polarization at less noble potential.

Figure 4 is a cross-sectional view of the surface for the electrodeposited specimens and characteristic X-ray images of Ni and Y. For the polarization at -2.0 and -2.2 V , thick layers are observed on the Ni substrate. The thicknesses of the layers formed at -2.0 and -2.2 V were about $30\text{--}100 \mu\text{m}$ and $120 \mu\text{m}$, respectively. It has been seen that the polarization at less noble potential led to an increase in the thickness of the deposition layer. It also appeared that these layers adhered well to the substrates. For the polarization at -1.8 V , the deposition layer has not been observed since the potential was slightly too noble. From the characteristic X-ray images it is clear that the layers formed at -2.0 and -2.2 V consisted of elemental Ni and Y, and they were widely distributed and uniform.

Figure 5 shows the X-ray surface diffraction patterns of the specimens electrodeposited at -2.0 and -2.2 V . For both specimens, diffraction peaks corresponding to

Fig. 3 Time dependence of cathodic current density during potentiostatic polarization in molten NaCl-KCl-2 mol% YCl_3 at 1073 K.

Fig. 4 Cross-sectional micrographs (Back Scattered Electron Image; BEI) and characteristic X-ray images of Ni and Y near the surface for the specimens electrodeposited at -1.8 , -2.0 and -2.2 V for 1.8ks. (D: deposit, S: substrate)

Fig. 5 X-ray surface diffraction patterns of the specimens electrodeposited in molten $\text{NaCl-KCl-2 mol\% YCl}_3$ at -2.0 and -2.2 V for 1.8 ks at 1073 K.

Ni-Y intermetallic compounds, i.e., Ni_3Y and Ni_5Y , were observed. This fact shows that electrodeposition of Y was successful and Ni and Y had diffused into each other and reacted to form the intermetallic compounds.

Figure 6 shows X-ray line scanned profiles and enlarged back scattered electron image (BEI) with EDX spectra for the deposit layer formed at -2.2 V. The back

scattered electron image was taken at the highest sensitivity as possible. The X-ray line profiles show that the distributions of Ni and Y are macroscopically uniform. However, the back scattered electron image indicates that there are some particles in the deposit and a thin layer lying next to the substrate. From the EDX analysis, it is found that Y content in these particles and in the layer is smaller than that in the matrix of the deposit layer. By considering Fig. 5, the particles and layer consist of Ni_5Y , and the matrix consists of Ni_3Y . Since Ni/Y atomic ratio of these two intermetallic compounds are similar, it is appeared that X-ray line scan profile could not distinguish the difference between Ni_3Y and Ni_5Y .

IV. Discussion

By the potentiostatic polarizations at -2.0 V and -2.2 V, electrodeposition of a Ni-Y intermetallic compound film, that was smooth and adhesive with the substrate, was successful. Deposition reactions and alloying between the deposit and the substrate proceeded as follows:

At first, electrochemical reduction of Y^{3+} in the molten salt proceeded according to eq. (1). Immediately, the deposited Y and Ni diffused into each other to form a Ni-Y intermetallic compound layer. In Fig. 6, there existed Ni_5Y along the substrate/deposit interface and among Ni_3Y matrix. It is thought that this structure was formed

Fig. 6 X-ray line scanned profiles of Ni and Y and enlarged back scattered electron image (BEI) with EDX spectra concerned with the specimen electrodeposited at -2.2 V for 1.8 ks.

by the following process; during the electrolysis, first, the deposit layer grew as Ni_5Y , and it changed into Ni_3Y layer according to eq. (2):

This reaction took place because Y was supplied from the depositing surface. Along these processes, Ni_3Y layer grew thick. The particles of Ni_5Y in the Ni_3Y matrix seen in Fig. 6 are residuals that have not completely reacted according to eq. (2).

As shown in Fig. 4, gourd-like interfaces were obtained in the case of polarization at -2.0 V. This is because the deposition of Y locally took place on the electrode surface. Thus, at places where the amount of Y deposition was large, the layer grew thick. In contrast, at -2.2 V, the deposition of Y were uniform as to form the thick and smooth layer due to the increase in current density for the deposition reaction.

The reason why a Ni_2Y intermetallic compound, whose formation was observed by Xie *et al.*,⁽³⁾ was not formed but Ni_3Y and Ni_5Y compounds were formed in this study seems to be that a higher temperature process induced more rapid diffusion of Ni and Y in the deposit layer. Namely, because the diffusion layer was thicker in spite of the fact that the amount of deposited Y was not larger, that led smaller Y/Ni content ratio to form Ni_3Y or

Ni_5Y .

V. Conclusions

From the above results, the following conclusions can be drawn:

The electrodeposition of Y and its alloying with the Ni substrate has been successfully done using potentiostatic polarization in the potential region less noble than -2.0 V in an equimolar NaCl-KCl melt containing 2 mol% YCl_3 at 1073 K. The alloying of deposited Y with substrate Ni led to the formation of a layer consisting of Ni_3Y and Ni_5Y intermetallic compounds. The polarization at less noble potential achieved thickening of the layer. The layer was smooth and had a good adhesion to the substrate. Such results suggest the possibility of surface alloying of Y by electrodeposition in molten salts at high temperature.

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